ATTENUATED EMBEDDED PHASE SHIFT PHOTOMASK BLANKS

FIELD OF THE INVENTION

The present invention is directed to attenuated embedded phase shift photomask blanks and in particular to attenuated phase shift mask (APSM) materials and processes.

BACKGROUND OF INVENTION

Phase shift masks are gaining attention as the next generation lithographic technique for microelectronic fabrication due to their capability to produce higher resolution images compared to the conventional binary photomasks. Among the several phase shifting schemes, the attenuating embedded phase shifter proposed by Burn J. Lin, Solid State Technology, January issue, page 43 (1992), the teaching of which is incorporated herein by reference, is gaining wider acceptance because of its ease of fabrication and the associated cost savings. There have been a number of variations associated with this scheme to improve the optical properties of the photomask, i.e. tunability of the optical transmission and resistance against photon irradiation and chemical treatments.

The attenuated phase shift mask (APSM) described in US Patent 5,897,977 to Carcia et al. consists of alternating layers of optically transmissive materials and optically absorbing materials. The advantage claimed by this process is that the phase shift and transmission can be controlled easily by adjusting the thickness of either or both of the layers. However, the deposition process is complicated since two different materials need to be deposited in an alternating sequence, which will increase the cost of the process and increase potential defects in the mask. Also, due to the different etching properties of the two materials, obtaining a smooth line edge by etching is difficult.

The APSM described in US Patent 5,939,227 to Smith consists of a multilayer of Si_xN_y and metal nitride. The advantage claimed by this process is both materials are chemically stable and etch selectivity is well defined. However, the deposition of this process is complicated since it requires two separate targets and a planetary sample stage, which increases the cost for manufacturing and again significantly increases potential defect levels.

A Zr-based APSM described in US 5935735 to Okubo et al., wherein the film had 2 to 15 % transmittance and less than 30 % reflectivity. The Zr-based film consisted of two or more multilayers with different optical properties to achieve the above transmittance and reflectivity. While this scheme provides good tunability, a multilayer structure may not provide good manufacturability. Also, due to the highly stable nature of Zr compounds, the RIE etch selectivity is inferior.

The APSM described in US Patents 5,942,356 and 6,153,341 to Mitsui et al., consists of molybdenum, silicon and nitride. The advantage claimed of this process is that it consists of a single material which gives good etch properties. Also, the material is stable during laser irradiation and acid treatment. However, the tunability of %T is not as flexible as the multilayer materials. Mitsui et al., does not incorporate a post-deposition treatment in their patent.

Herein we describe a method to fabricate, through deposition and post deposition treatment, a phase shift photomask that has tunable optical transmission, coupled with stable optical properties during usage (photon exposure and chemical treatments) of the photomask.

The present invention provides a phase shift photomask with a small surface roughness and low defect density by reducing the particulates produced during the deposition process.

We have also discovered that when the phase shift mask or phase shift mask blank is annealed to a temperature higher than room temperature under an atmosphere which contains oxygen at more than 10^{-3} torr partial pressure, a film structure can be produced that is stable against photon irradiation and chemical treatments for photomask fabrication.

SUMMARY OF THE INVENTION

A broad aspect of the present invention comprises an attenuating embedded phase shift photomask blank capable of producing a phase shift of 180° with an optical transmission of at least 0.001% at a selected lithographic wavelength, having chemical and optical durability and flexible optical transmission tunability.

In another aspect, the invention comprises a process of making an attenuating embedded phase shift photomask, which process comprises the steps of depositing a thin film phase shifting material.

In another aspect, the invention comprises a process of making an attenuating embedded phase shift photomask, which uses a composite target with high material density and high discharge stability during the deposition process.

In another aspect, the invention comprises a process for stabilization and improvement of the optical characteristics of the phase shifting material.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other objects, features and advantages of the present invention will become apparent upon a consideration of the following detailed description and the invention when read in conjunction with the drawing Figures, in which:

Fig. 1 is a bar graph showing the Root mean square (RMS) roughness of the deposition using three different targets. The RMS roughness is measured over a 2000 Å x 2000 Å scan area of an Atomic Force Microscope (DI5000, tapping mode). The RMS roughness is 0.80, 0.39 and 0.20 nm for films deposited with Dual target, Hot pressed target, and HIP target, correspondingly.

Fig. 2 is a summary of the RBS analysis of various films deposited under single target configuration.

Fig. 3A is a graph showing the relationship between the transmission (%T) at 193 nm wavelength and the N_2 flow (sccm) for the composite cathode($Si_{0.7}(TiSi_2)_{0.1}$). All were deposited at 15 sccm Ar flow.

Fig. 3B is a graph showing the relationship between refractive index (n) at 193 nm wavelength and the N_2 flow (sccm) for the same samples in Fig. 3A.

Fig. 3C is a graph showing the relationship between extinction coefficient (k) at 193 nm wavelength and the N_2 flow (sccm) for the same samples in Fig. 3A.

Fig. 4 is a plot of the Transmission and Reflectivity as a function of wavelength from 190 to 900 nm.

Fig. 5 XPS analysis of the deposited thin films. (a) surface and bulk compositions of the thin films before and after annealing. (b) A depth profile plot of embodiment 9. The sputter time is proportional to the film thickness, zero minute indicates the surface.

Fig. 6 is a graph showing the relationship between the transmission (%T) at 193 nm wavelength and the laser dosage (kJ/cm^2). Two samples, annealed and unannealed, are plotted together for comparison. The annealed sample shows an

improved stability compared to the unannealed sample. The laser power density was 1.75 mJ/cm^2/pulse at 100 Hz frequency.

Fig. 7 is a summary of the %T changes after executing three different post-deposition processes (air anneal, N$_2$ anneal, and oxygen plasma treatment) and %T changes after laser irradiation.

Fig. 8 is a graph showing the relationship between the transmission (%T) at 193 nm wavelength and the duration time of film exposed to a mixture of H$_2$SO$_4$:H$_2$O$_2$=10:1 at 95 °C (also known as piranha solution). The %T change was 0.19 % over 60 min immersion in the solution.

Fig. 9 is a summary of the RBS analysis and optical properties of films deposited with various oxygen partial pressures.

Fig. 10 is a summary of the RBS analysis for various samples deposited under dual target configuration.

Fig. 11A is a graph showing the relationship between the transmission (%T) at 193 nm wavelength and the power (watt) applied to the Ti cathode for the deposition of Si$_w$Ti$_x$N$_y$ and Si$_w$Ti$_x$N$_y$O$_z$ using co-sputtering from two pure targets: silicon nitride (Si$_3$N$_4$) and titanium (Ti).

Fig. 11B is a graph showing the relationship between the refractive index (n) at 193 nm wavelength and the power (watt) applied to the Ti cathode for the same samples in Fig. 11A.

Fig.11C is a graph showing the relationship between the extinction coefficient (k) at 193 nm wavelength and the power (watt) applied to the Ti cathode for the same samples in Fig.11A.

DETAILED DESCRIPTION

A process is discovered for fabricating photomask blanks that produces phase shifting films having tunable optical characteristics (%T,n and k) (T is the transmission; n is the index of refraction; and k is the extinction coefficient) with 180° phase shift at 193 nm and with significantly enhanced exceptional stability against laser irradiation and chemical treatment. The phase shifting films comprise of silicon and a metal and nitrogen and/or oxygen. The metal can be an element from the groups II, IV, V, transition metals, lanthanides and actinides. An example will be given for titanium as the metal. The invention comprises a thin phase shifting film ($Si_wTi_xN_y$ or $Si_wTi_xN_yO_z$, where w is in the range 0.1 to 0.6, x is in the range 0.01 to 0.2, y is in the range 0 to 0.6, z is in the range 0 to 0.7.) deposited on a substrate (quartz, Al_2O_3, etc) with a thin oxygen rich layer on the surface and the methods for forming the films and enhancing their characteristics.

1.   Deposition

The initial thin film can be deposited by sputter deposition (RF, DC magnetron, AC magnetron, pulsed bipolar DC magnetron, RF diode sputtering, or other sputter deposition methods familiar to those skilled in the art) from either a single target of a composite material ($Si_{1-x}Ti_x$, with x in the range 0.01 to 0.5) or two or more targets of different compositions (for example, Si_3N_4 and Ti targets, or $Si_{1-x}Ti_x$ and Ti targets). Variation in composition of the composite targets or individual variation of power and deposition time of the pure targets produces changes in film composition. Reactive sputtering with nitrogen and oxygen provides further capability to adjust the relative compositions of Si, Ti, and N and O, and thus the optical characteristics of the film. The substrate stage can be either stationary or planetary for the single target, and planetary for the multitarget with rotation speed adjusted accordingly.

Specifically, a RF magnetron sputtering was used for a single target $(Si_{0.7}(TiSi_2)_{0.1})$ deposition and a RF and DC magnetron co-deposition was used for dual target $(Si_3N_4$ and Ti) deposition.

2. Post-deposition modification of film structure

The surface layer of the deposited film becomes oxygen rich when exposed to air but is still unstable against radiation and chemical treatment. Subsequent heat treatment (air annealing) produces a much enhanced stability. X-Ray Photoelectron Spectroscopy (XPS) results show about 2 % increase in the oxygen concentration of the surface after annealing at 225 °C in air atmosphere. This surface enhancement can be accomplished by either air annealing at elevated temperature or other gas mixtures or plasma treatment in an oxidizing environment.

The enhanced stability can be attributed to the fact that the change of optical properties during irradiation is due to the photon induced oxidation under oxidizing atmosphere. Thus, by pre-oxidizing the surface with the described methods, the optical properties of the deposited film show an enhanced stability against irradiation. Details of the post-deposition modification is described in section 5 (A).

3. Optical properties

The optical properties (index of refraction (n), and extinction coefficient (k)) were determined using an n&k spectrophotometer in the range of 190 to 900 nm. The transmission at 180° phase shift was calculated by using these n and k values.

4. Fabrication process of the $Si_{0.7}(TiSi_2)_{0.1}$ Target

A special target for the composite cathode is utilized. Instead of mixing Ti and Si elements, a mixture of $TiSi_2$ and Si was used. It was reported, US Patent 5,686,206, paragraph 6, line 56-67, that the discharge during sputter deposition becomes unstable

as the silicon to metal ratio increases. In particular, for Mo and Si, the discharge became unstable for targets with Si larger than 95 mol percent. The problem is due to low conductivity at the target surface since SiN_x, which is an insulator, is formed during the process.

By utilizing the described process, we were able to increase the metal to silicon ratio increased from 1/9 to 1/7 (i.e., 28% increase of the metal to silicon ratio), thereby decreasing the amount of SiN_x layer. The target consists of 10 atomic percent of Ti in the form of $Si_{0.7}(TiSi_2)_{0.1}$ instead of $Ti_{0.1}Si_{0.9}$.

Also, to reduce the particulate formation during the deposition, the target can be made using a HIP (hot isostatic pressing) process. The HIP process typically yields an increase in the density of the target as compared to the conventional hot pressing process. The improved densification varies with material properties but generally leads to, a reduction of particulate levels in the sputter deposited films which reduces the defects and surface roughness, as well as improving the target machinablility and strength. Hot pressed targets of this material exhibited a density of 2.085 which is 75% of the theoretical density of 2.78. HIP targets of this material possess densities of 96-98% of theoretical values without interconnecting voids, resulting in significant improvements to the strength and particulate levels of the target.

To demonstrate the improvement of the surface roughness, the Atomic Force Mircroscope data is shown in Figure 1. The RMS roughness was taken over 2000 Å x 2000 Å area for three different deposition conditions. The first was the dual target deposition (Hot pressed target $(Si_{0.7}(TiSi_2)_{0.1})$ in RF with Hot pressed Ti target in DC), the second was the conventional Hot pressed target $(Si_{0.7}(TiSi_2)_{0.1})$, the third was a HIP processed target $(Si_{0.7}(TiSi_2)_{0.1})$. The thickness of the film was 670 Å for all three samples. The dual target deposition was the roughest (0.8 nm), then the Hot pressed target (0.39 nm), and the HIP processed target gave smoothest surface RMS roughness (0.20 nm) with 15 % uncertainty of the measurement.

5. Examples

(A). $Si_w Ti_x N_y$ or $Si_w Ti_x N_y O_z$ photomask blanks prepared by single target

1) Processing gas Ar/N_2

Thin films composed of $Si_w Ti_x N_y$ or $Si_w Ti_x N_y O_z$ by using a $Si_{0.7}(TiSi_2)_{0.1}$ target were deposited, with the substrate in a rotating holder with planetary motion or positioned under the target without planetary motion. Sputtering was carried out in an argon/nitrogen mixture with 1.0~ 5.0 mT Ar partial pressure. Ultra high purity gases were used for both Ar and N_2 (99.999 %) and the background pressure of the chamber was < 9.0 x 10^{-7} torr. The thin film was deposited by RF magnetron sputtering from a five inch diameter target with a power of 450 W. Under the above conditions, the deposition rate was typically 0.6 to 1.6 Å/sec.

Prior to sputtering, the target was presputtered in 5 mT Ar for 5 min at 450 W. Then 5 min of presputtering was performed under the deposition condition of the thin film to precondition the surface of the target. After presputtering, the substrates were immediately loaded through a load lock chamber into the deposition chamber and deposition was carried out. The film thickness ranged between 400 to 2000 Å depending on the deposition conditions. Figure 2 summarizes the film deposition conditions and the resulting composition obtained from RBS analysis.

Fig 3A. summarizes the %T calculated for films at 180° phase shift versus the N_2 flow. The %T increases with increasing N_2 flow from 6-9 sccm, beyond which little change is observed with higher N_2 flow. The RBS result shows that the amount of N_2 incorporated into the film increases with N_2 flow until about 9 sccm, then changes little with further increase of N_2 flow. Figures 3B and 3C summarize the n and k values as a function of N_2 flow and deposition pressure, respectively. The RBS analysis shows an increasing oxygen concentration in the film as the deposition pressure increases. The optical properties, n and k are dependent on the N and O concentration of the film and

the density of the film. Higher deposition pressure reduces the film density and reduces the n value.

The reason for increasing O incorporation as the deposition pressure increases is thought to be the following. The increasing pressure reduces the kinetic energy of the ions and radicals in the plasma (shorter mean free path), and thus makes background oxygen easier to stick to the surface as materials are being deposited.

Fig 4 is an example of the transmission and reflectivity curves measured from the n&k analyzer. The sample was deposited at 1 mT, Ar flow 15 sccm, N_2 flow 9 sccm, thickness 679 Å, followed by an air anneal at 225 °C for 15 min. For this thickness, the phase shift calculated from the n and k value at 193 nm is 183.1 degrees. The transmission at 193 nm was measured as 5.72 %. The film composition measured by RBS is Si 39 atomic %, Ti 3.3 atomic %, N 57 atomic %, O < 1 atomic %.

Figure 5(a) is an XPS analysis of the surface and bulk concentration of two embodiments before and after post-deposition process. Deposition condition for embodiment 9 is 1 mT, N_2 flow - 9 sccm, and RF power - 450 W, film thickness 679 Å. Deposition condition for embodiment 10 was 5 mT, N_2 flow - 9 sccm, and RF power - 450 W, film thickness 890 Å. In this example, the process involves 225 °C annealing in air atmosphere for 15 minutes. The oxygen concentration of the surface increases about 2 % after the annealing for both embodiments. While the oxygen concentration increase of the bulk film was not detected, it is possible a small amount (below the XPS detection limit, <1 %) bulk oxygen increase could have occurred and affect the optical property. Figure 5(b) is a depth profile of the chemical concentration of embodiment 9. The sputter time increase corresponds to the film thickness increase.

Figure 6 summarizes the change of %T at 193 nm as a function of Ar-F laser at 193 nm (Lambda Physik LPX 120) irradiation with and without the post-deposition process. The samples were prepared at deposition pressure 1 mT of Ar with N_2 at 9 sccm, RF power of 450 W. The film thickness corresponded to 679 Å. In order to

perform irradiation studies, two films under the identical conditions were deposited on the substrate. The second film was annealed in air atmosphere at 225 °C for 15 minutes. These films were both irradiated with laser power density of 1.75 mJ/cm^2/pulse at 100 Hz frequency. The unannealed film shows significant radiation instability (>0.5% increase in transmission) especially during the first kJ of irradiation. The huge Transmission increase after the first kJ is no longer present in the annealed sample. The total transmission change at a dose of 5.4 kJ/cm^2 is 0.27 %. Note that there is transmission change caused by annealing (0.42%).

Other examples of post-deposition process include oxygen plasma treatment and annealing under nitrogen atmosphere. The comparison of the two with air anneal is shown in Figure 7. The increase of the %T after oxygen plasma treatment is comparable to the air annealing at 225 °C for 15 minute. The %T increase is smaller for the N_2 annealing at 225 °C for 15 min. compared to the other two processes. Also, the N_2 annealing improves the stability of the film to some degree due to the finite amount of oxygen background pressure. However, the stability is inferior to the air annealed result. For example, in Figure 7, the %T of the air annealed sample increased 0.27 % over laser dosage of 5.4 kJ/cm^2, while the %T of the N_2 annealed sample increased 0.32 % over dosage of 2.2 kJ/cm^2, already exceeding the %T for the air annealed sample at less than half of the laser dose.

Figure 8 summarizes the change of %T at 193 nm as a function of immersion time in a cleaning solution of sulfuric acid and hydrogen peroxide(H_2SO_4:H_2O_2=10:1, 95 °C), this solution is typically used for stripping photoresists in manufacturing line, also known as piranha solution. The deposition and post-deposition process is identical to the film described in Figure 6. The total change of %T is 0. 19 % over 60 min of immersion. This excellent stability ensures a compatibility of the material with the standard photomask manufacturing process.

2) Processing gas $Ar/N_2/O_2$

Thin films composed of $Si_wTi_xN_yO_z$ by using a $Si_{0.7}(TiSi_2)_{0.1}$ target were deposited, with the substrate in a rotating holder with planetary motion or positioned under the target without planetary motion. Sputtering was carried out in an argon/nitrogen/oxygen mixture processing gas with 1.0 mT Ar partial pressure (Ar flow at 15 sccm) and 0.30 mT N_2 partial pressure (N_2 flow at 5.55 sccm). Oxygen was leaked in with a Gransville-Phillips precision leak valve to maintain a constant O_2 partial pressure ranging from 0.10 to 0.20 mT. The thin film was deposited by RF magnetron sputtering from a five inch diameter target with a power of 450 W. Under the above conditions, the deposition rate was typically 0.75 to 1.6 Å/sec.

Prior to sputtering, the target was presputtered in 5 mT Ar for 5 min at 450 W. Then 5 min of presputtering was performed under the deposition condition of the thin film to precondition the surface of the target. After presputtering, the substrates were immediately loaded through a load lock chamber into the deposition chamber and deposition was carried out. The film thickness ranged between 400 to 2000 Å depending on the deposition conditions.

By adjusting the oxygen to nitrogen, transmission as high as 20% can be achieved at 193 nm for film thickness corresponding to 180 degree phase shift. Such wide transmission window provides the possibility of extending the operation wavelength down to 157 nm. Figure 9 summarizes the film deposition conditions, optical properties (%T at 180 degree phase shift, n, and k), and the resulting composition obtained from RBS analysis.

B. $Si_wTi_xN_y$ where as w = 0.1~0.6, x=0.01~0.2, y=0.3~0.6 and $Si_wTi_xN_yO_z$ where as w = 0.1~0.6, x=0.01~0.2, y=0~0.6, and z=0~0.7 photomask blanks prepared by multitarget.

Thin films composed of $Si_wTi_xN_y$ and $Si_wTi_xN_yO_z$ by using Si_3N_4 and Ti targets were deposited, with the substrate in a rotating holder with planetary motion. Sputtering was carried out in an argon/nitrogen gas mixture at 1 - 2mT deposition pressure with Ar

flow at 15 sccm and N_2 flow at 6 sccm. The Si_3N_4 target was sputtered with an RF magnetron at a fixed power of 900 W and the Ti target was sputtered with a dc magnetron using power ranging from 0 to 200 W. Both targets were 5 inch in diameter. Under the above conditions, the deposition rate was typically 1.7 to 2.1 Å/sec.

Prior to sputtering, both targets were simultaneously presputtered in 5 mT Ar for 5 min at 900 W and 400 W for the RF and DC cathodes respectively. Then 5 min of presputtering was performed under the deposition conditions of the thin film to precondition the surface of the targets. After the presputtering, immediately the substrates were loaded through a load lock chamber into the deposition chamber and deposition was carried out. The film thickness ranged from 400 to 2000 Å depending on the deposition parameters.

Figure 10 summarizes the film deposition conditions and the resulting composition obtained from RBS analysis. Figure 11A summarizes the %T calculated for films at 180° phase shift versus the Ti target power. The %T decreases as the Ti target power increases. The increase of Ti power incorporates more Ti into the film (see Figure 10) which reduces the %T. The %T is tunable by varying the Ti concentration. Figure 11B and Figure 11C summarize the n and k values as a function of Ti target power respectively.

While this invention has been described in terms of certain embodiment thereof, it is not intended that it be limited to the above description, but rather only to the extent set forth in the following claims. The embodiments of the invention in which an exclusive property or privilege is claimed are defined in the appended claims. The teaching of all references cited herein, are incorporated herein by reference.